

Systematic Field-Theory for the Hard-Core One-Component Plasma

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Abstract

An accurate and systematic equation of state for the hard-core one-component plasma (HCOCP) is obtained. The result is based on the Hubbard-Schofield transformation which yields the field-theoretical Hamiltonian, with coefficients expressed in terms of equilibrium correlation functions of the reference hard-core fluid. Explicit calculations were performed using the Gaussian approximation for the effective Hamiltonian and known thermodynamic and structural properties of the reference hard-core fluid. For small values of the plasma parameter Γ and packing fraction the Debye-Hückel result is recovered, while for $\Gamma \gg 1$, the excess free energy F_{ex} and internal U_{ex} energy depend linearly on Γ . The obtained expression for U_{ex} is in a good agreement with the available Monte Carlo data for the HCOCP. We also analyse the validity of the widely used approximation, which represents the free energy as a sum of the hard-core and electrostatic part.

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1 Introduction

The one component plasma (OCP) is one of the basic models in the field of charged systems. The OCP model is formulated as a system of point particles, interacting via the Coulomb potential, which move in a uniform neutralizing background. It has found important physical applications in a variety of fields ranging from terrestrial physics, through important technological applications to cosmology [1, 2, 3, 4]. As a reference model it is used in many areas of soft condensed matter, such as colloidal and polyelectrolyte solutions, e.g. [5, 6, 7, 8], etc. All thermodynamic properties of the OCP depend only on the dimensionless plasma parameter $\Gamma = l_B/a_c$, where $l_B = e^2/k_B T$ is the Bjerrum length (e is the charge of the particles, k_B is the Boltzmann's constant, T is the temperature) and $a_c = (3/4\pi\rho)^{1/3}$ is the ion-sphere radius with $\rho = N/\Omega$ being the concentration of particles (N is the number of particles, Ω is the volume of the system). Using a field-theoretical approach, a fairly accurate and simple expression for the equation of state of the OCP has been obtained within the Gaussian approximation for the effective Hamiltonian [9]; contrary to previous calculations, e.g. [10, 11], this gives a correct behavior for the thermodynamic functions in the full range

of Γ (see [9] and references therein) and does not have fitting parameters as e.g. in [11, 12]. In [13] field-theoretical calculations for the equation of state, going beyond the Gaussian approximation, have been performed, showing that corrections to the Gaussian theory are rather small.

A closely related model – the hard-core one component plasma (HCOCP) incorporating a hard core repulsion between ions – gives a more satisfactory description of the short-range electrostatic correlations. The importance of this model follows also from the fact that it belongs to the class of the so-called primitive models used to describe molten salts [14], electrolytes [15], liquid metals [16, 17, 18] and charged colloidal solutions [19, 20, 21]. The mean spherical approximation (MSA) [22] was applied to account for both the hard-core and electrostatic interactions in this system [23, 24]. Although it has an analytical solution, it exhibits sometimes unphysical negative contact values for the pair correlation function, which has to be remedied by a rescaling procedure [25, 26, 27]. A mixed Percus-Yevick/hypernetted chain integral equation also has been used [28] and it was observed that it fits better the simulation results [29] than the MSA and cluster expansion [30, 31]. The former however does not have an analytical formulation. An analytical equation of state for the HCOCP has been proposed in [32], as a simple generalization of the hole-corrected Debye-Hückel theory [10], which in addition to the correlation hole around charged particles takes into account the hard-core repulsion. This was used afterwards to develop a generalized van der Waals theory [33]. The basic physical idea exploited in this theory is that due to the strong electrostatic repulsion a “hole” appears around a charged particle from which all other particles are expelled. Outside the hole the electrostatic interactions are not very strong and may be described on the Debye-Hückel level; the size of the hole is found self-consistently. Although being physically appealing, this theory does not give a satisfactory description for large values of the plasma parameter Γ for the OCP [10], and is also not accurate for the HCOCP for large packing fractions η (for $\eta = 0.4$ the deviations from MC data for the internal energy reach 24% [32]). Recently *an exact* low-density expansion for the free energy of the HCOCP has been obtained [34]. This however can not be applied in the case of strong electrostatic interaction, i.e. for large Γ .

In the present study we develop a theory which allows to derive a fairly accurate and simple equation of state for the HCOCP in the whole range of Γ from the Debye-Hückel limit $\Gamma \ll 1$ up to the limit of strong coupling $\Gamma \gg 1$. It reproduces within 1-3% accuracy the available Monte Carlo (MC) data for $0.2 < \Gamma < 70$. Larger deviations occur in the region where the MC data are not very accurate (see the discussion below). As in the case of the OCP [9] we use the Hubbard-Schofield transformation which yields a field-theoretical Hamiltonian for the HCOCP with coefficients expressed in terms of equilibrium correlation functions of a reference hard-core fluid. Although we perform the explicit calculations within the Gaussian approximation for the effective Hamiltonian, one can go beyond the Gaussian approximation using the standard perturbation technique, provided the structural properties of the reference hard-core fluid are known. Since the obtained equation of state is in good agreement with available MC data we use it to address the problem of additivity of the hard-core and electrostatic contributions to the excess free energy. This seems to be important since it is usually assumed that these contributions are additive (e.g. [35]) and the range of validity of such approximation has not been studied yet.

The rest of the paper is organized as follows: in Sec.2 we briefly sketch the Hubbard-Schofield approach which yields the field-theoretical Hamiltonian for the HCOCP. In Sec.3 we derive the equation of state within the Gaussian approximation for the effective Hamiltonian,

and compare the theoretical findings with available Monte Carlo data. In that section we also analyse the accuracy of the widely used approximation in which the excess free energy is written as a sum of the hard-core and electrostatic part. In the Conclusion we summarize our findings.

2 Field-Theoretical Hamiltonian for HCOCP

We start from the HCOCP Hamiltonian with omitted ideal part which may be written as follows ($\beta^{-1} = k_B T$):

$$H = \frac{1}{2} \beta^{-1} \sum'_{\mathbf{k}} \nu_k (\rho_{\mathbf{k}} \rho_{-\mathbf{k}} - \rho) + H_{hc} \quad (1)$$

where the first term in the right-hand side of (1) refers to the Coulomb interactions, written in terms of collective density variables,

$$\rho_{\mathbf{k}} = \frac{1}{\sqrt{\Omega}} \sum_{j=1}^N e^{-i\mathbf{k}\mathbf{r}_j} \quad (2)$$

where \mathbf{r}_j denotes coordinate of j -th particle,

$$\nu_k = 4\pi l_B / k^2 \quad (3)$$

is the Fourier-transformed Coulomb potential and H_{hc} describes the hard-sphere interaction. Summation in (1) is to be performed over the wave vectors $\mathbf{k} = \{k_x k_y k_z\}$ with $k_i = 2\pi l_i / L$ ($i = x, y, z$), where l_i are integers, $L^3 = \Omega$, and the prime over the sum denotes that the term with $\mathbf{k} = 0$ is excluded [36].

2.1 Hubbard-Schofield transformation

The configurational integral may be written in terms of the configurational integral of the reference (hard-sphere liquid) system Q_R [37, 38, 39] as:

$$Q = \left\langle \exp \left\{ -\frac{1}{2} \sum'_{\mathbf{k}} \nu_k (\rho_{\mathbf{k}} \rho_{-\mathbf{k}} - \rho) \right\} \right\rangle_R Q_R \quad (4)$$

where $\langle (\dots) \rangle_R = Q_R^{-1} \int d\mathbf{r}^N (\dots)$ denotes the averaging over the reference system. In accordance with the Hubbard-Schofield scheme [37] we use the identity:

$$\exp \left(\frac{1}{2} a^2 x^2 \right) = \frac{1}{\sqrt{2\pi a^2}} \int_{-\infty}^{+\infty} \exp \left(-\frac{1}{2} y^2 / a^2 + ixy \right) dy$$

and arrive after some algebra at:

$$Q = Q_R \int \prod'_{\mathbf{k}} c_{\mathbf{k}} d\varphi_{\mathbf{k}} \exp \left\{ -\frac{1}{2} \sum'_{\mathbf{k}} \nu_k^{-1} \varphi_{\mathbf{k}} \varphi_{-\mathbf{k}} \right\} \left\langle \exp \left\{ i \sum'_{\mathbf{k}} \rho_{\mathbf{k}} \varphi_{-\mathbf{k}} \right\} \right\rangle_R \quad (5)$$

where $c_{\mathbf{k}} = (2\pi\nu_k)^{-1/2} \exp\{\nu_k \rho / 2\}$, and where the integration is to be performed under restriction, $\varphi_{-\mathbf{k}} = \varphi_{\mathbf{k}}^*$ ($\varphi_{\mathbf{k}}^*$ is the complex conjugate of $\varphi_{\mathbf{k}}$) [40]. Applying the cumulant theorem [41] to the factor $\langle \exp \{ i \sum'_{\mathbf{k}} \rho_{\mathbf{k}} \varphi_{-\mathbf{k}} \} \rangle_R$ one obtains:

$$\begin{aligned}
Q &= Q_R \int \prod_{\mathbf{k}}' c_{\mathbf{k}} d\varphi_{\mathbf{k}} e^{-\mathcal{H}}, \quad \text{with} \\
\mathcal{H} &= \sum_{n=2}^{\infty} \Omega^{1-\frac{n}{2}} \sum_{\mathbf{k}_1, \dots, \mathbf{k}_n}' u_n(\mathbf{k}_1, \dots, \mathbf{k}_n) \varphi_{\mathbf{k}_1} \dots \varphi_{\mathbf{k}_n} \\
u_2(\mathbf{k}_1, \mathbf{k}_2) &= \frac{1}{2} \delta_{\mathbf{k}_1+\mathbf{k}_2, 0} \left\{ \frac{1}{\nu_k} + \langle \rho_{\mathbf{k}_1} \rho_{-\mathbf{k}_1} \rangle_{cR} \right\} \\
u_n(\mathbf{k}_1, \dots, \mathbf{k}_n) &= -i^n \frac{\Omega^{\frac{n}{2}-1}}{n!} \langle \rho_{\mathbf{k}_1} \dots \rho_{\mathbf{k}_n} \rangle_{cR} \quad n > 2
\end{aligned} \tag{6}$$

here $\langle \dots \rangle_{cR}$ denotes *cumulant* average [41] for the reference hard sphere fluid system. Note that (6) gives the field-theoretical expression for the partition function with, $\varphi_{\mathbf{k}}$ being the Fourier components of the scalar field $\varphi(\vec{r})$ [42]. The coefficients of the effective Hamiltonian (6) are expressed in terms of the correlation functions of the reference hard-core fluid. Using definitions of correlation functions of fluids [43] and definitions of the cumulant averages [41], one can *directly* evaluate $\langle \rho_{\mathbf{k}_1} \dots \rho_{\mathbf{k}_n} \rangle_{cR}$ (and thus the coefficients $u_n(\mathbf{k}_1, \dots, \mathbf{k}_n)$). It is straightforward to show that $\langle \rho_{\mathbf{k}_1} \dots \rho_{\mathbf{k}_n} \rangle_{cR}$ may be expressed in terms of the Fourier transforms of the correlation functions h_2, h_3, \dots, h_n of the reference system, defined as [39]

$$h_2(\mathbf{r}_1, \mathbf{r}_2) \equiv g_2(\mathbf{r}_1, \mathbf{r}_2) - 1 \tag{7}$$

$$h_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \equiv g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - g_2(\mathbf{r}_1, \mathbf{r}_2) - g_2(\mathbf{r}_1, \mathbf{r}_3) - g_2(\mathbf{r}_2, \mathbf{r}_3) + 2, \text{ etc.}, \tag{8}$$

where $g_l(\mathbf{r}_1, \dots, \mathbf{r}_l)$ are l -particle correlation functions [43]. In particular the second-order cumulant $\langle \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \rangle_{cR}$ may be written as:

$$\langle \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \rangle_{cR} = \rho \left[1 + \rho \tilde{h}_2(\mathbf{k}) \right], \tag{9}$$

and the Fourier transform of the function $\tilde{h}_2(\mathbf{k})$ is related to the direct correlation function $\tilde{c}_2(\mathbf{k})$

$$\tilde{h}_2(\mathbf{k}) = \tilde{c}_2(\mathbf{k}) / [1 - \rho \tilde{c}_2(\mathbf{k})], \tag{10}$$

for which an explicit analytical expression is known [44].

2.2 Gaussian approximation for the effective Hamiltonian

Now we concentrate on the Gaussian part of the effective Hamiltonian, i.e. we skip all the terms with a power of the field larger than two. The accuracy of this approximation has been critically examined in Ref.[13] for the OCP without hard-core interactions by perturbatively calculating higher-order terms. It was found that higher order terms contribute very little to the free energy and that the Gaussian approximation is in fact excellent over the whole range of coupling parameters. One can therefore assume, and this is indeed borne out by our comparison with Monte-Carlo data below, that the Gaussian approximation should also be quite good for the present case. Using (10) and (9) we write for this case:

$$Q = Q_R \int \prod_{\mathbf{k}}' d\varphi_{\mathbf{k}} \frac{\exp(\nu_k \rho / 2)}{\sqrt{2\pi\nu_k}} \exp \left\{ -\frac{1}{2} \sum_{\mathbf{k}}' \varphi_{\mathbf{k}} \varphi_{-\mathbf{k}} \left(\frac{1}{\nu_k} + \frac{\rho}{1 - \rho \tilde{c}_2(\mathbf{k})} \right) \right\} \tag{11}$$

Performing (Gaussian) integration over $\varphi_{\mathbf{k}}$ we arrive after some algebra at [40]:

$$Q = Q_R \prod_{k_z > 0}' \frac{\exp(\nu_k \rho)}{\nu_k} \left(\frac{1}{\nu_k} + \frac{\rho}{1 - \rho \tilde{c}_2(\mathbf{k})} \right)^{-1} \tag{12}$$

Taking the logarithm of the configuration integral one obtains the free energy, and since the analytical expression for $\tilde{c}_2(\mathbf{k})$ is available [44], no additional approximation is, in principle, required. This leads, however, to an expression which is to be evaluated numerically. We note that owing to the long-range nature of the Coulombic interactions, the main contribution to the free energy comes from the long-wave modes of the density fluctuations, which correspond to small k . Therefore only the small- k behavior of the direct correlation function is important. This suggests to approximate $\tilde{c}_2(\mathbf{k})$ by a truncated expansion

$$\tilde{c}_2(\mathbf{k}) \simeq \tilde{c}_2(0) - \tilde{c}_2(0)''k^2 + \dots, \quad (13)$$

which correctly behaves at small k . As we show in what follows, only wave-vectors with $k < k_0$ contribute to the configuration integral, thus we apply the approximation (13) for the interval $0 < k < k_0$. By numerical evaluation of the free energy using the full expression for $\tilde{c}_2(\mathbf{k})$, we convinced ourselves that deviations of the quadratic form from the actual $\tilde{c}_2(\mathbf{k})$ at larger k do not noticeably affect the results[46]. We therefore do not require k and k_0 to be small since the particular behavior of $\tilde{c}_2(\mathbf{k})$ for large k is not important. On the other hand, the quadratic approximation allows to obtain an analytical equation of state for the HCOCP that reproduces fairly well the available Monte Carlo data. With (13) one can write for the configurational integral:

$$Q = Q_R \prod'_{k_z > 0} \frac{\exp(\nu_k \rho)}{\nu_k} \left(\frac{1}{\nu_k} + \frac{\rho}{1 - \rho \tilde{c}_2(0)} - k^2 \frac{\rho^2 \tilde{c}_2(0)''}{(1 - \rho \tilde{c}_2(0))^2} \right)^{-1} \quad (14)$$

The most accurate estimate for $\tilde{c}_2(0)$ may be found, using $\tilde{c}_2(0) = \tilde{h}_2(0)/(1 + \rho \tilde{h}_2(0))$ from (10) and the relation for the isothermal compressibility $\chi_R^{-1} = \rho(\partial P_R / \partial \rho)_\beta$ [43], where P_R is the pressure of the reference system [47]:

$$1 + \rho \tilde{h}_2(0) = \rho k_B T \chi_R \equiv Z_0 \quad (15)$$

The value of Z_0 follows from the fairly accurate Carnahan-Starling free energy of hard-sphere fluid [48]:

$$\frac{\beta F_{hc}}{N} = \frac{4\eta - 3\eta^2}{(1 - \eta)^2}, \quad (16)$$

where $\eta = \frac{1}{6}\pi\rho d^3$ is the packing fraction and d is the diameter of the spheres; this yields Z_0 as a second derivative of F_{hc} with respect to density:

$$Z_0 = (1 - \eta)^4(1 + 4\eta + 4\eta^2 - 4\eta^3 + \eta^4)^{-1} \quad (17)$$

Using the Wertheim-Thiele solution for the direct correlation function $c_2(r)$ [44] and definition of $\tilde{c}_2(0)''$ from Eq.(13) one obtains:

$$\tilde{c}_2(0)'' = \frac{1}{2} \int r^2 c_2(r) d\mathbf{r} = -(\pi d^5 / 120)(16 - 11\eta + 4\eta^2)(1 - \eta)^{-4} \quad (18)$$

With $\tilde{c}_2''(0)$ from (18) and $\tilde{c}_2(0) = (Z_0 - 1)/(\rho Z_0)$ from (10) and (15) we arrive at the following expression for the configurational integral

$$Q = Q_R \prod'_{k_z > 0} \exp(\rho \nu_k) (\rho \nu_k Z_0 + \Theta)^{-1} \quad (19)$$

where $\Theta = 1 - 4\pi l_B (\rho Z_0)^2 \tilde{c}_2''(0)$.

3 Equation of state for the HCOCP

3.1 Equation of state and its accuracy

Now we show that within the Gaussian approximation to the effective Hamiltonian, one obtains rather accurate equation of state for HCOCP provided that an appropriate value of the “ultraviolet cutoff” in the \mathbf{k} -space is employed. From (19) we find for the excess free energy of the HCOCP:

$$-\beta F_{ex} = \ln(Q) = -\beta F_{hc} + \frac{1}{2} \sum'_{\mathbf{k}} [\rho \nu_k - \ln(\rho \nu_k Z_0 + \Theta)] \quad (20)$$

Now we argue that the summation in (20) should be carried out over a *finite* number of the wave-vectors \mathbf{k} . In this we follow the Debye theory of the specific heat of solids (e.g. [49]). Namely, we assume that the total number of degrees of freedom in the system, $3N$, should be equal to the total number of *physically different* modes with the wave-vectors \mathbf{k} within the spherical shell of radius k_0 in the \mathbf{k} -space. The number of modes is twice the number of the wave-vectors, since for each \mathbf{k} one has a sine and cosine mode (the amplitude of the \mathbf{k} -th mode is a complex number) [50]. Thus we obtain:

$$2 \frac{\Omega}{8\pi^3} 4\pi \int_0^{k_0} k^2 dk = 3N \quad (21)$$

where the factor $\Omega/8\pi^3$ appears when the integration in \mathbf{k} -space is used instead of summation. From (21) follows that

$$k_0 = (9\rho\pi^2)^{1/3}$$

A similar Debye-like scheme to find the cutoff k_0 was first proposed for plasma in [51], where a somewhat different value of the cutoff wave-vector was reported. Using k_0 as obtained above we write:

$$\begin{aligned} \frac{\beta F_{ex}}{N} &= \frac{\beta F_{hc}}{N} + \frac{1}{2} \frac{\Omega}{8\pi^3} \frac{4\pi}{N} \int_0^{k_0} k^2 dk [\ln(\rho \nu_k Z_0 + \Theta) - \rho \nu_k] \\ &= \frac{\beta F_{hc}}{N} + \frac{9}{4} \int_0^1 x^2 dx \left[\ln \left(\Theta + \frac{b\Gamma Z_0}{x^2} \right) - \frac{b\Gamma}{x^2} \right], \end{aligned} \quad (22)$$

where $x = k/k_0$, so that $\rho \nu_k = 4\pi l_B \rho / (k_0 x)^2 = b\Gamma/x^2$ (see (3) for the definition of ν_k), and where we define the constant $b = \frac{2}{3} \left(\frac{2}{\pi^2} \right)^{1/3}$. The last integral is easily evaluated and yields for the excess free energy

$$\frac{F_{ex}}{k_B T N} = \frac{4\eta - 3\eta^2}{(1 - \eta)^2} + \frac{3}{4} \left[\ln(\Theta + b\Gamma Z_0) - b\Gamma \left(3 - \frac{2Z_0}{\Theta} \right) \right] - \frac{3}{2} \left(\frac{b\Gamma Z_0}{\Theta} \right)^{\frac{3}{2}} \arctan \left(\sqrt{\frac{\Theta}{b\Gamma Z_0}} \right) \quad (23)$$

with

$$\Theta = 1 + \frac{6}{5} \frac{e^2}{dk_B T} \frac{\eta^2(1 - \eta)^4(16 - 11\eta + 4\eta^2)}{(1 + 4\eta + 4\eta^2 - 4\eta^3 + \eta^4)^2} \quad (24)$$

and for the excess internal energy, $U_{ex} = -T^2 \partial(F_{ex}/T)/\partial T$ of the HCOCP

$$\frac{U_{ex}}{k_B T N} = \frac{9}{4} \left[\frac{b\Gamma Z_0}{\Theta} - b\Gamma - \left(\frac{b\Gamma Z_0}{\Theta} \right)^{\frac{3}{2}} \arctan \left(\sqrt{\frac{\Theta}{b\Gamma Z_0}} \right) \right]. \quad (25)$$

For $\eta = 0$, Eqs.(23,25) recover the corresponding result for the one component plasma [9].

As it follows from (23) and (25), for $\Gamma \rightarrow 0$ and $\eta \rightarrow 0$ the Debye-Huckel behavior is obtained. In the opposite limit $\Gamma \gg 1$ and for any packing fraction η Eqs.(23) and (25) demonstrate a linear behavior on Γ . The leading term for this case is $-A\Gamma$, where the constant A reads:

$$A = \frac{9}{4}b = \frac{3}{2} \left(\frac{2}{\pi^2} \right)^{1/3} = 0.881 \dots$$

This is fairly close to the constant $A = 0.899 \dots$ of the fits for the OCP (see e.g.[52, 53]).

For arbitrary values of η and Γ we compare our analytical expression for the excess internal energy (25) with the available MC data for the HCOCP (Fig.1). Fig.2 shows the relative error of the analytical expression (25). As it follows from Fig.1 and Fig.2 the equation of state is fairly accurate in full range of plasma parameters for which MC data are available. For $\Gamma > 1$ the relative error does not exceed 1 – 3% for all values of packing fraction and plasma parameter. For $\Gamma > 10$ one observes the linear behavior and deviation from the numerical data for this range of Γ less than 1%.

The maximal deviation of the analytical expression from the MC data occurs for $0.2 < \Gamma < 1$. In this range of the plasma parameter the deviation is about 5% with the maximal one of 12% at the smallest value $\Gamma = 0.2$. It should be noted however, that such deviation occurs for Γ , where the method of MC loses its accuracy. Moreover, we expect that for very small packing fraction, $\eta = 0.001$, where the maximal deviation is observed, the contribution to the internal energy due to the hard-core interactions may not exceed 1%. Therefore for this η the difference between U_{ex} of the HCOCP and U_{ex} of the OCP is less than 1%. It has been already shown that the analytical equation of state for the OCP (which follows from (25) for $\eta = 0$) has the accuracy of 8% [9]. Thus we expect that the accuracy of our equation of state may not be worse than 9% for these values of η ; the observed deviation of 12% seems to be the manifestation of the low accuracy of MC for this range of parameters.

3.2 Additivity of the hard-core and electrostatic components of the free energy.

With the equation of state obtained we can analyse the accuracy of the widely used approximation for the excess free energy, which represents this as a sum of the hard-core and electrostatic component, $F_{hc} + F_{ex,OCP}$ (see e.g. [35]). The validity of this approximation may be checked by the direct comparison of the excess free energy of the HCOCP $F_{ex,HCOCP}$ and the above sum. For $F_{ex,HCOCP}$ we use our equation of state (23) and equation of state for OCP from [9] (this expression for $F_{ex,OCP}$ may be obtained from Eq.(23) for $\eta = 0$). For $F_{ex,hc}$ we use the Carnahan-Starling Eq.(16). In Fig.3 we compare the "complete" equation of state (solid lines) with the approximate, based on the assumption of additivity of the hard-core and electrostatic parts (dashed lines). As it follows from Fig.3 for small Γ the values of the free energy from the "complete" and approximate equations of state may differ significantly; they may even have different signs. The relative difference becomes smaller with increasing Γ (see inset to Fig.3) and decreasing packing fraction. For $\Gamma > 50$ the approximation reaches the reasonable accuracy: the error does not exceed 5% for all η . For small packing fractions, $\eta < 0.1$ one has the same accuracy already for $\Gamma > 10$.

4 Results and Discussion

A "first-principle" equation of state for the classical hard-core one component plasma is obtained that has a correct Debye-Huckel behavior at the limit of small plasma parameter Γ and small packing fractions ($\Gamma \rightarrow 0, \eta \rightarrow 0$). It demonstrates a linear dependence on Γ for any packing fraction if $\Gamma \gg 1$. The obtained coefficient 0.881 at the linear leading term in this case is close to the corresponding coefficient 0.899 found for the one component plasma in the Monte Carlo simulations. The simple analytical expression for the excess internal energy reproduces the available MC data with an accuracy of 1–3% for the most range of Γ and η . The maximal deviation of 12% is observed for small Γ and η , where the MC method is not very accurate, and we argue that such deviation does not reflect the accuracy of our equation.

To derive the equation of state we apply the Hubbard-Schofield transformation to obtain the field theoretical Hamiltonian for the HCOPC and use the Gaussian approximation. The Gaussian approximation assumes that one can neglect all terms in the effective Hamiltonian which contain the power of field higher than two. As it was shown by the field theoretical calculations for the case of the one component plasma (without the hard-core) [13], the corrections to the Gaussian theory are rather small, and we expect that the same is true for the system of interest. Physically, this implies that the higher-order coefficients in the field theoretical Hamiltonian are smaller than that at the second order of the field. In this case the contribution to the field integral from the field-amplitude domain where the higher-order terms dominate is small: The main contribution comes from the domain where the Gaussian term prevails. Generally, the Gaussian approximation fails near the critical point, where the Gaussian term of the effective Hamiltonian becomes small and even vanishes [39]. For the HCOCP we do not expect any criticality and thus the Gaussian approximation is expected to be valid.

To obtain the analytical expression for the equation of state we also approximate the Fourier transform of the direct correlation function of the reference hard-core system $\tilde{c}_2(\mathbf{k})$ by its small- k expansion. Although such approximation deviates from the actual dependence of $\tilde{c}_2(\mathbf{k})$ at larger k , this does not eventually affect the equation of state: Owing to the long-range nature of the Coulombic interactions, only the small- k behavior of $\tilde{c}_2(\mathbf{k})$ is important; this is correctly reproduced by the approximation.

We also analyse the validity of the widely used approximation, where the free energy of the HCOCP is represented as a sum of the hard-core and electrostatic component. We show that such approximation is rather accurate for small packing fraction and large plasma parameter. In the opposite case of large η and small Γ the excess free energy may not be adequately represented by a sum of a hard-core and electrostatic part.

Thus we conclude that in general case one has to use the complete equation of state. The proposed one possesses a reasonable accuracy for the whole range of parameters for the system of interest.

References

- [1] M.Baus and J.P.Hansen, Phys.Rep., **59**, 1 (1980)
- [2] S.Ichimar, H.Iyetomi and S.Tanaka, Phys.Rep., **149**, 91 (1987)

- [3] N.H.March and M.P.Tosi, *Coulomb Liquids* (Academic, London, 1984)
- [4] N.H.March and M.P.Tosi, *Atomic Dynamics in Liquids* (Wiley, New York, 1976)
- [5] M.J.Stevens, and M.O.Robins, *Europhys.Lett.*, **12**, 81 (1990).
- [6] H.Loewen, *Phys.Rep.*, **237**, 249 (1994).
- [7] R.Penfold, B.Jonsson, and S.Nordholm, *J.Chem.Phys.*, **99**, 497 (1993).
- [8] N.V.Brilliantov, D.V.Kuznetsov, and R.Klein, *Phys.Rev.Lett.*, **81**, 1433 (1998).
- [9] N.V.Brilliantov, *Contrib.Plasma Phys.*, **38**, 489 (1998).
- [10] S.Nordholm, *Chem.Phys.Lett.*, **105**, 302 (1984).
- [11] G.Stringfellow, H.E.DeWitt, and W.L.Slattery, *Phys.Rev.A*, **41**, 1105 (1990).
- [12] B.Brami, J.P.Hansen, and F.Joly, *Physica A*, **95**, 505 (1979).
- [13] A.G.Moreira and R.R.Netz, *Eur.Phys.J. D* **8**, 145 (2000).
- [14] B.Hafskjold and G.Stell *The Liquid State of Matter*, edited by E.W.Montroll and J.L.Lebowitz (North-Holland, Amsterdam, 1982)
- [15] C.W.Outwaite, in *Statistical Mechanics*, Vol.2, *A Specialis Periodical Report*, edited by K.Singer (Chemical Society, London, 1975)
- [16] J.B.Hayter, R.Pynn, and J.B.Suck, *J.Phys.F.* **13**, L1 (1983)
- [17] H.B.Sing and A.Holz, *Phys.Rev.A* **28**, 1108 (1983)
- [18] R.V.Gopala Rao and R.Das, *Ind.J.Phys.A* **60**, 295 (1986)
- [19] C.Caccamo, *J.Chem.Phys.* **91**, 4902 (1989)
- [20] L.Belloni, *J.Chem.Phys.* **88**, 5143 (1988)
- [21] A collection of relevant references one can find in *Faraday Discuss. Chem.Soc.*, **76** (1983).
- [22] J.L.Lebowitz and J.Percus, *Phys.Rev.* **144**, 251 (1966)
- [23] E.Waisman, and J.Lebowitz, *J.Chem.Phys.*, **56**, 3086 (1972); **56**, 3093 (1972).
- [24] R.G.Palmer, and J.D.Weeks, *J.Chem.Phys.*, **58**, 4171 (1973).
- [25] J.P.Hansen and J.B.Hayter, *Mol.Phys.* **46**, 651 (1982).
- [26] B.V.R.Tara, R.Kesavamoorthy, and A.K.Arora, *Mol.Phys.* **57**, 369 (1986).
- [27] B.Svensson and B.Jonsson, *Mol.Phys.* **50**, 489 (1983).
- [28] F.Lado, *Mol.Phys.* **31**, 1117 (1976)

- [29] J.P.Hansen and J.J.Weis, Mol.Phys. **33**,1379 (1977)
- [30] H.C.Anderson and D.Chandler, J.Chem.Phys. **57**,1918(1972); **57**,1930(1972)
- [31] L.Verlet and J.J.Weis, Mol.Phys. **28**,665 (1974)
- [32] R.Penfold and S.Nordholm, J.Chem.Phys. **95**,2048 (1991)
- [33] R.Penfold and S.Nordholm, J.Chem.Phys. **96**,3102 (1992)
- [34] R.R.Netz, and H.Orland, Eur.Phys.J. E **1**, 67 (2000).
- [35] Y.Levin, M.C.Barbosa, and M.N.Tamashiro, Europhys.Lett., **41**, 123 (1998).
- [36] The term with $\mathbf{k} = 0$ conceals with the terms describing the self-interaction of the compensating background and interaction of the background with particles.
- [37] J.Hubbard and P.Schofield, Phys.Lett., **A40**,245 (1972)
- [38] N.V.Brilliantov and J.P.Valleau, J.Chem.Phys., **108**,1123 (1998).
- [39] N.V.Brilliantov, Phys.Rev.E, **58**,2628 (1998).
- [40] To obtain Eq.(5) we take into account that $\rho_{\mathbf{k}}\rho_{-\mathbf{k}} = (\rho_{\mathbf{k}}^c)^2 + (\rho_{\mathbf{k}}^s)^2$ where $\rho_{\mathbf{k}}^c$ and $\rho_{\mathbf{k}}^s$ are respectively the real (cosine) and imaginary (sine) parts of $\rho_{\mathbf{k}}$. Similar relation for $\varphi_{\mathbf{k}}\varphi_{-\mathbf{k}}$ is used, to obtain Eq.(12).
- [41] R.Kubo, J.Phys.Soc.Jap., **17**,1100 (1962)
- [42] Such Hamiltonians are typical for magnetic systems, where $\varphi(\vec{r})$ is the spin-field, see e.g. S.Ma, *Modern Theory of Critical Phenomena* (Benjamin, New York, 1976)
- [43] C.G.Gray and K.E.Gubbins, *Theory of molecular fluids*, Clarendon Press, Oxford, 1984.
- [44] The direct correlation function for the hard sphere fluid reads [45]: $c_2(r) = 0$, when $r \geq d$ and $c_2(r) = (1 - \eta)^{-4} \left\{ -(1 + 2\eta)^2 + 6\eta \left(1 + \frac{1}{2}\eta\right)^2 (r/d) - \frac{1}{2}\eta(1 + 2\eta)^2(r/d)^3 \right\}$ when $r < d$, where d is the diameter of the hard spheres. For $\tilde{c}_2(\mathbf{k})$, which may be easily found from $c_2(r)$ we do not need the complete expression.
- [45] M.S.Wertheim, Phys.Rev.Lett., 1963, v.10, N8, 321; E.Thiele, J.Chem.Phys., 1963, v.39, 474.
- [46] The maximal deviation between the free energy evaluated with the full expression for $\tilde{c}_2(\mathbf{k})$ and with the quadratic expansion is approximately 0.5% and occurs at a packing fraction of $\eta = 0.4$ and a plasma parameter $\Gamma = 0.4$. For all other values of the parameter, the deviations are smaller.
- [47] The value of $\tilde{c}_2(0)$ may be obtained directly as the zero-order moment of the Wertheim-Thiele solution for $c_2(r)$ [44] of the hard-sphere fluid. This is however based on the approximate Percus-Yevik closure [43] and occurs to be less accurate than that related to $\tilde{h}_2(0)$, with $\tilde{h}_2(0)$ taken from the Carnahan-Starling compressibility. This happens because the Carnahan-Starling semiempirical equation of state [48] is more accurate than those found from the Wertheim-Thiele solution [43].

- [48] N.F.Carnahan and K.E.Starling, J.Chem.Phys., 1969, v.51, N2, 635.
- [49] J.M.Ziman, *Principles of the Theory of Solids* (Clarendon Press,Oxford,1964)
- [50] Note that the restriction $\varphi_{-\mathbf{k}} = \varphi_{\mathbf{k}}^*$ does not reduce the total number of *physically different* modes, since the modes with the wave-vectors \mathbf{k} and $-\mathbf{k}$ correspond to that spreading in the opposite directions.
- [51] A.S.Kakljugin, *Teplofizika Visokih Temperatur*, **23**,217 (1985)
- [52] B.Jancovici, J.Stat.Phys., **17**,357 (1977)
- [53] J.P.Hansen Phys.Rev.A, **8**,3096 (1973)

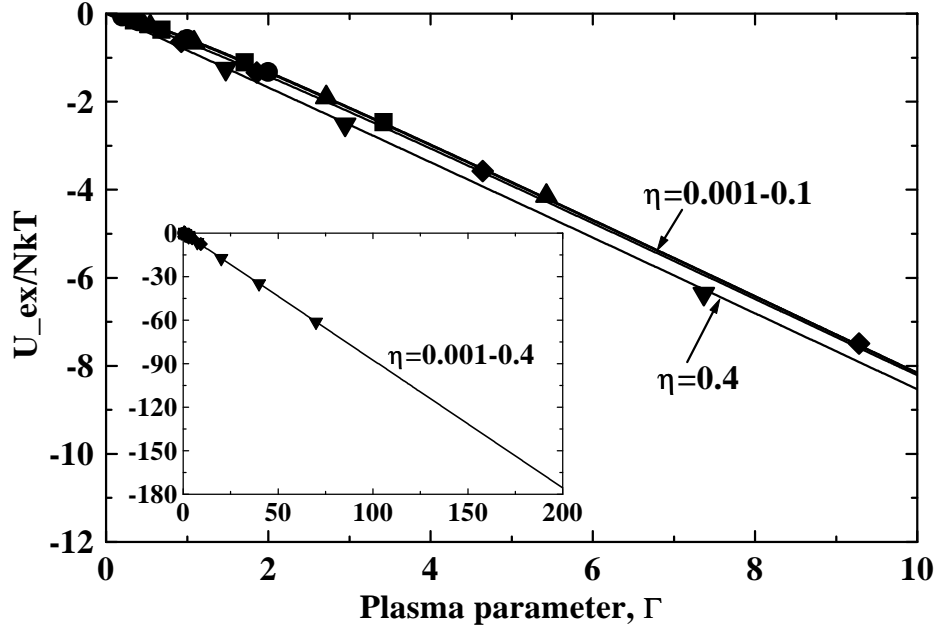


Figure 1: Shows the dependence of the excess internal energy of the HCOCP $U_{ex}/Nk_B T$ on the plasma parameter $\Gamma = l_B/a_c$ ($l_B = e^2/k_B T$, $a_c = (3/4\pi\rho)^{1/3}$) for different values of the packing fraction $\eta = (\pi/6)d^3\rho$. The curves from top to bottom correspond to $\eta = 0.001$, $\eta = 0.005$, $\eta = 0.020$, $\eta = 0.100$ and $\eta = 0.400$, respectively. Points give the Monte-Carlo data [29, 32]: circles correspond to $\eta = 0.001$, squares to $\eta = 0.005$, triangles to $\eta = 0.020$, diamonds to $\eta = 0.100$ and down triangles to $\eta = 0.400$, respectively. In the inset the same dependence is shown for larger range of Γ .

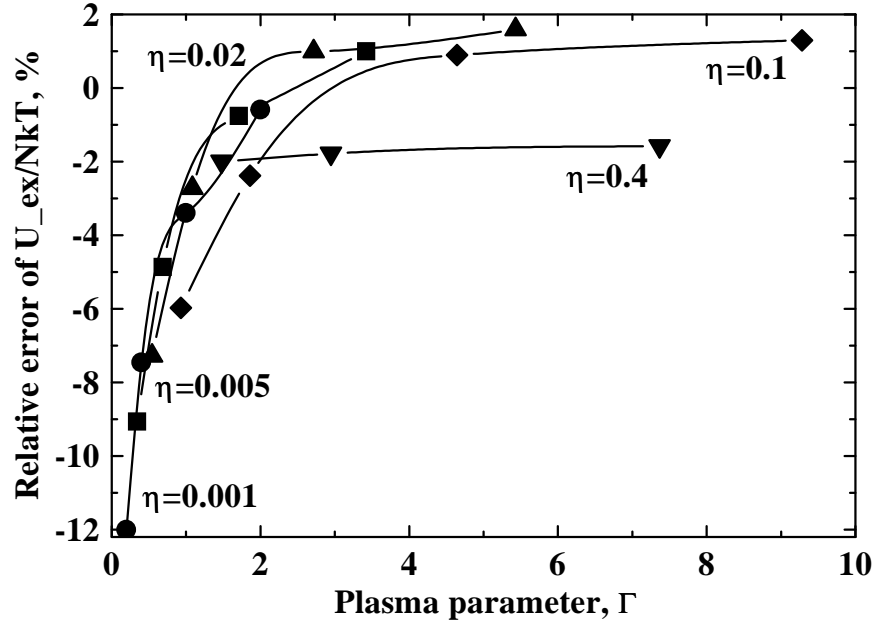


Figure 2: Gives the relative error of the analytical expression (25) for excess internal energy of the HCOCP $U_{ex}/Nk_B T$ as a function of the plasma parameter Γ . Notations are the same as in Fig.1.

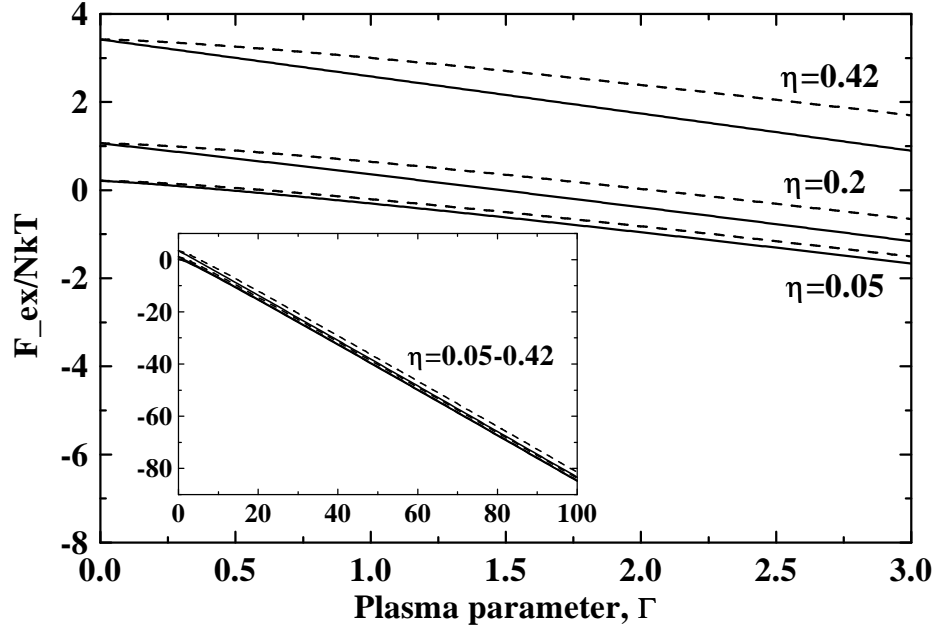


Figure 3: Compares the "complete" equation of state, $F_{ex,HCOCP}$ (23), for the free energy of the HCOCP (solid lines) with the approximate one, given as the sum of the free energy of the point particle OCP and that of the hard-core fluid, $F_{ex,OCP} + F_{hc}$ (dashed lines). The curves from top to bottom correspond respectively to $\eta = 0.42$, $\eta = 0.2$ and $\eta = 0.05$. In the inset the same dependence is shown for larger range of Γ .